Tentative explanation for the kinetic compensation effect in doped catalysts

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Abstract

The kinetic parameter compensation effect displayed by heterogeneous catalysts may occur when the global reaction is a combination of competing reactions which show the same mechanism and take place on different groups of active centres, each group showing different activation energy and pre-exponential factor values. In this study, a simple procedure is described for employing apparent kinetic data (ln(A) and Ea) that show a compensation effect in order to calculate the activation energies and pre-exponential factors (proportional to the population densities) of active centres that present equal reaction mechanisms in dual site catalysts. The procedure was used to reproduce apparent kinetic data taken from the literature and obtained from experiments with doped-catalysts prone to dual-site catalytic behaviour. The fittings obtained in all cases were very good. The population density of active centres with Ea_2 activation energy showed constant growth with the increase in doping agent content, whereas that of the active centres originally present in the undoped catalysts (Ea_1) showed varying trends.

Keywords: Compensation effect; reaction rate; activation energy; heterogeneous catalysis

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Introduction

The dependence of the rate of many chemical reactions on temperature is usually expressed by the Arrhenius equation:

$$k = A \times \exp\left(\frac{-Ea}{R \times T}\right)$$

(1)

where k is the reaction rate constant, Ea is the activation energy, A is the pre-exponential factor, R is the universal gas constant (8.314 J/mol) and T is the absolute temperature. In a series of closely related chemical reactions such as those produced by a given set of reactants on the surface of different catalysts, where each catalyst displays a different pair of Arrhenius parameters (A, Ea), it is often found that there is a linear relation between the natural logarithm of the pre-exponential factors and the activation energies:

$$\ln(A) = \alpha + \frac{Ea}{R \times \beta}$$

(2)

where α and β are constants. This phenomenon has been known since the beginning of the 20th century [1] as the *compensation effect* [2, 3] of the kinetic parameters. In the literature many attempts have been made to explain this effect in relation to heterogeneous catalytic reactions, a review of which is presented in the excellent work by Liu and Guo [4]. There is a mathematical explanation which postulates that random errors in kinetic data generate an apparent compensation effect (sometimes termed the statistical compensation effect) [5]. In such cases, when the Arrhenius parameters have been obtained by ordinary linear regression of $\ln(k_i)$ *vs* $1/T_i$, data (standard procedure) the so-called *isokinetic* temperature (parameter β in equation (2)) is very close to the harmonic mean temperature, which is defined as:

$$T_{hm} = \frac{n}{\sum_{i=1}^{n} \frac{1}{T_i}}$$

(3)

where n is the number of data points subjected to linear regression. Thus, this mathematical approach is only valid when the value of β obtained by the linear fitting of $\ln(A)$-Ea data to equation (2) is close to T_{hm} and the values of k obtained by means of equation (1) at a given temperature are very similar for the different (A, Ea) pairs. In the

absence of these restrictions, the compensation effect must have a physical explanation rather than a mathematical one.

Within the framework of the Transition State Theory [6], the kinetic compensation effect is equivalent to the enthalpy-entropy compensation. According to Benson [7] this compensation is easily understood by associating decreases in enthalpy (exothermic changes) with "tighter" binding and consequently with less entropy ("freedom of motion"). To date this has been the most widely used argument for explaining the compensation effect on physical grounds.

Another physical explanation is that proposed by Nicholas [8] and Bagg [2], which assumes that the compensation effect occurs when the global reaction is a combination of competing reactions that take place on different groups of active centres, each group displaying different values of activation energy and a different pre-exponential factor. In his pioneering work on the compensation effect [1] Constable, who worked with data on alcohol dehydrogenation over reduced copper achieved by Palmer and himself [9], demonstrated the compensation effect by assuming that a random strain of active centres on the surface of an amorphous catalyst is proportional to the decrease in activation energy promoted by such active centres. In this way he was able to derive an exponential expression for the distribution of active centres with different activation energies on the catalyst surface, $F(Ea)=C\times exp(h\times Ea)$, that neatly explains the compensation effect. Therefore he was the first person to recognize the heterogeneity of the catalyst surface as the possible cause of kinetic compensation, although he developed his theory for catalysts with random heterogeneity and so logically it cannot be applied to catalysts with *tailor-made* heterogeneities such as doped catalysts.

This specific type of compensation effect is justifiably considered as "not interesting" by Liu and Guo [4], since using a real complex rate equation instead of an overall rate equation would eliminate the compensation effect. However, to obtain individual reaction rate equations for each group of active centres is very often an almost impossible task. In this work we offer a simple way to obtain the kinetic parameters of active centres in dual site catalysts, in case they present a unique and simple reaction mechanism, by assuming strictly bimodal distributions associated to two different activation energies. The strategy is tested with compensation effect kinetic data reported in the literature for doped catalysts.

Numerical demonstration of the compensation effect in dual site catalysts

For catalysts with random population densities of two types of active centres displaying a unique reaction mechanism in which the reaction rate is proportional to a function of the gas concentrations, the following equation can be used:

$$k = k_1 + k_2 = A_1 \times \exp\left(-Ea_1\middle/RT\right) + A_2 \times \exp\left(-Ea_2\middle/RT\right)$$

(4)

where k is the experimentally obtained apparent reaction rate constant, k_1 and k_2 are the reaction rate constants for both types of active centres and A_1 and A_2 are pre-exponential factors that depend on the population density of the active centres associated to the activation energies Ea_1 and Ea_2, respectively. In heterogeneous catalysis one can add reaction rates that occur in parallel, which individually are a product of a reaction rate constant (k_1, k_2) and a function of gas concentration, to obtain the global reaction rate. Therefore, in equation (4) the gas concentration dependences of the individual reaction rates are assumed to be identical. This assumption includes all active centres that display equal reaction mechanisms (or reaction orders) but differing reaction rate constants. To prove that equation (4) can lead to a compensation effect in Ea and ln(A), the values of k were obtained for random values of A_1 and A_2 ($A_1 = 75,000 \pm 43,500$, $A_2 = 3.00 \pm 1.74$) at different values of Ea_1 and Ea_2. Figure 1 shows the results. As can be seen, all the points obtained for fixed values of Ea_1 and Ea_2 are arranged in more or less "noisy" but clear compensation trends. In the cases selected and presented in Figure 1 the trends are not strictly linear but display some curvature, as is often experimentally found [10]. According to the literature the noise in autocorrelation plots is possibly caused by the existence of a more or less narrow distribution of activation energies within the peaks considered as single Arrhenius peaks [11], as stated in the common distributed activation energy models.

The average regression coefficient ($<R^2>$), obtained by averaging the values of R^2 derived from the different linear regressions (ln(k) *vs*. 1/T) used to construct each compensation effect trend, varies with the difference in activation energy between the two types of active centres, as illustrated in the inset plot in Figure 1. This tendency implies that the curvature of the Arrhenius plots (ln(k) *vs*. 1/T) increases with the increase in the difference between Ea_1 and Ea_2, as has been mathematically proved by Bagg [2].

Testing the dual site-based compensation effect in doped-catalysts

Provided that the compensation effect really is caused by pure dual site catalysts with different population densities of active centres that present equal reaction mechanisms, equation (4) can be used to find the values of A_1 and A_2, which are proportional to the population densities of both types of active centres, from the experimental kinetic data obtained from catalysts that show a compensation effect. To test this point we have used kinetic data taken from the literature related to metal-doped or metal oxide-doped catalysts that clearly show compensation effects [12-15]. In principle such catalysts are prone to dual-site catalytic behaviour [16]. The data obtained from the literature were fitted to equation (4) via the following procedure. First, the values of k in the range of temperatures applied in the reported experiments were computed by means of equation (1) for all the catalysts by using the (A, Ea) values reported in the different works (see Figure 2). This produced a set of k values for the different temperatures and catalysts that were then fitted to equation (4) to obtain the values A_1 and A_2, for each catalyst, and those of Ea_1 and Ea_2, which are common to all the catalysts in a series. The objective of the fitting was to minimize the average error for the different temperatures and catalysts, which is defined as:

$$\varepsilon = \left\langle \ln \left(\frac{}{} \right) - \ln \left({}_1 + k_2 \right) \right\rangle \tag{5}$$

where k is calculated from equation (1) and k_1+k_2 from equation (4). To perform the fitting procedure the Microsoft Solver complement of Microsoft Excel was used.

Table 1 shows the results of the fitting procedure for the different processes and catalysts analysed in this work. For each series of doped catalysts, the values of k at a given temperature are spread over a wide range. This simple fact, together with the conspicuous differences between the values of the isokinetic temperature (β) and those of the harmonic mean temperature (T_{hm}) rule out the existence of statistical compensation effects for the catalysts in Table 1. The last column of Table 1 shows the average regression coefficients ($<R^2>$) obtained with the different linear regressions ($\ln(k_1+k_2)$ $vs.$ $1/T$) used to construct each compensation effect trend. In all of the cases the values are over 0.99, which justifies the use, in the original works, of a single site apparent reaction rate. The activation energies obtained for both types of active centres

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(Ea$_1$ and Ea$_2$) in each compensation trend are, in general, similar to the lowest and highest activation energies within the compensation trend.

Figures 2 to 7 show the results of applying equation (4) to the compensation trends reported in the literature [12-15]. Figure 2 represents the original compensation trend together with the calculated values of A and Ea obtained from the linear regressions (ln(k$_1$+k$_2$) *vs.* 1/T); Figures 3 to 6 show the variation of A$_1$ and A$_2$ with the amount of doping agent; and Figure 7 shows the goodness of the fitting process by comparing the values of ln(k) (equation (1)) with those of ln(k$_1$+k$_2$) (equation (4)).

Figure 3 shows the results for a series of potassium-doped Co$_3$O$_4$ catalysts supported on stainless steel wire meshes recently employed in the catalytic decomposition of N$_2$O [12]. As can be seen in Figures 2 and 7, the fitting procedure permitted a good reproduction of both the compensation trend and the values of k. A$_1$ and A$_2$ display different trends (Figure 3). Whereas A$_2$ shows a regular increase with the increment in potassium content in the catalysts (K/Co molar ratio), A$_1$ increases up to K/Co~0.015 and then decreases abruptly down to zero at K/Co~0.03. This somewhat peculiar trend is responsible for the maximum of reactivity at K/Co values of around 0.02, as detected in [12] and in previous works [17]. It appears that a small amount of doping agent produces an increase in the population densities of both types of active centres, i.e., those already present in small amounts on the surface of the undoped catalyst and those created by the synergy between potassium and cobalt. With higher amounts of doping agent only the second group of active centres prevails.

Similar results were obtained for the nickel and cobalt-based catalysts doped with Ag$_2$O [13, 15], as can be seen in Figures 4 and 5. For these catalysts Figures 2 and 7 show even better fittings to equation (4) than in the former case. This doping agent was used with different catalysts (NiO [15] and Co$_3$O$_4$/Al$_2$O$_3$ [13]) in different processes (H$_2$O$_2$ decomposition [15] and CO oxidation [13]) but it still produced a similar trend in the values of A$_1$ to that obtained for the K-doped catalysts (Figures 4 and 5). This trend therefore must also be a characteristic of Ag$_2$O doping. As in the former case, the value of A$_2$ was zero for the undoped catalyst but it grew constantly as greater amounts of Ag$_2$O were added to the catalyst. Examination of Figures 4 and 5 shows that the maximum value of A$_1$ shifts to lower Ag$_2$O contents as the calcination temperature of the catalysts (Table 1) increases.

Finally, the results for a silver-doped NiO-based catalyst used in the steam reforming of methane (Figure 6) show a trend that one would expect with any kind of doping, i.e. A_1 decreases steadily and A_2 increases as the silver content increases. The fitting process also revealed excellent agreements between the experimental and calculated values (Figures 2 and 7). This was the only series of catalysts that presented a value of Ea_1 lower than that of Ea_2 (Table 1). As can be seen in Figure 8 for a catalyst taken from the series in Figure 3, when doping decreases the apparent activation energy ($Ea_2 < Ea_1$) the catalyst is activated in the low temperature region, where the value of k_1 is insignificant. The opposite trend is observed when doping produces an increase in the apparent activation energy: the catalyst is activated in the high temperature region as can be seen also in Figure 8 for a catalyst taken from the series in Figure 6.

It should be pointed out that this procedure is only applicable to strict dual site catalysts whose different active centres truly display the same reaction mechanism. The trends depicted in Figures 3 to 6 are sensible and reasonable, but in no case can be considered valid unless they are validated by a previous characterisation of the catalyst's surface. Thus, the application of the dual site-based compensation effect strategy described in this work to characterise doped catalysts is awaiting a final validation that will be the object of a future work.

Conclusions

In this work, a simple procedure is described for calculating the activation energies and the pre-exponential factors (proportional to population densities) of active centres in dual site catalysts from apparent kinetic data (ln(A) and Ea) that present a compensation effect. The procedure was applied to apparent kinetic data taken from the literature. The data were obtained for doped-catalysts which are prone to dual-site catalytic behaviour. The fittings obtained in all cases were very good and the trends obtained for the values of A_1 and A_2, depending on the amount of doping agent added, are justifiable on physical grounds, though further validation is needed from catalyst surface characterisation.

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Captions to figures

Figure 1. Compensation effect associated to dual site catalysis with random populations of active centres (A_1 = 75,000 ± 43,500, A_2 = 3.00 ± 1.74). Inset plot: variation of the average regression coefficient ($<R^2>$) obtained with the different linear regressions used to build each compensation effect trend with the relative difference of activation energies

Figure 2. Results of fitting data reported in [12-15] to equation (4). Compensation effect

Figure 3. Results of fitting data reported in [12] to equation (4). Variation of A_1 and A_2 with the K/Co molar ratio

Figure 4. Results of fitting data reported in [15] to equation (4). Variation of A_1 and A_2 with the Ag_2O content

Figure 5. Results of fitting data reported in [13] to equation (4). Variation of A_1 and A_2 with the Ag_2O content

Figure 6. Results of fitting data reported in [14] to equation (4). Variation of A_1 and A_2 with the Ag content

Figure 7. Results of fitting data reported in [12-15] to equation (4). Comparison of experimental k values with k_1+k_2 in the analysed temperature interval

Figure 8. Variation of k_1, k_2 and k with temperature for the catalyst prepared in [12] at K/Co=0.022 and tested for the catalytic decomposition of N_2O in the presence of oxygen, and for the catalyst prepared in [14] with 0.1 wt.% Ag and tested for the steam reforming of methane

Tables

Table 1. Kinetic parameters obtained via equation (4) for different doped catalysts reported in the literature

Ref.	Process	Catalyst type (calcination temperature)	T_{hm} (°C)	β (°C) (R^2, eq. 2)	Ea_1 (kJ/mol)	Ea_2 (kJ/mol)	$<R^2>$ eq. 1
[12]	N_2O decomposition	K-doped Co_3O_4 (400°C)	564.2	813.1 (0.9787)	102.6	37.9	0.9906
[15]	H_2O_2 decomposition	Ag_2O-doped NiO (300°C)	311.7	528.7 (0.9828)	55.6	29.2	0.9999
		Ag_2O-doped NiO (500°C)	311.7	453.2 (0.9501)	54.6	21.5	0.9994
[13]	CO oxidation	Ag_2O-doped Co_3O_4/Al_2O_3 (800°C)	426.9	953.2 (0.9983)	26.1	10.2	0.9998
[14]	CH_4 steam reforming	Ag-doped NiO/γ-Al_2O_3 (450°C)	777.8	877.4 (0.9995)	77.1	133.1	0.9996

Figures
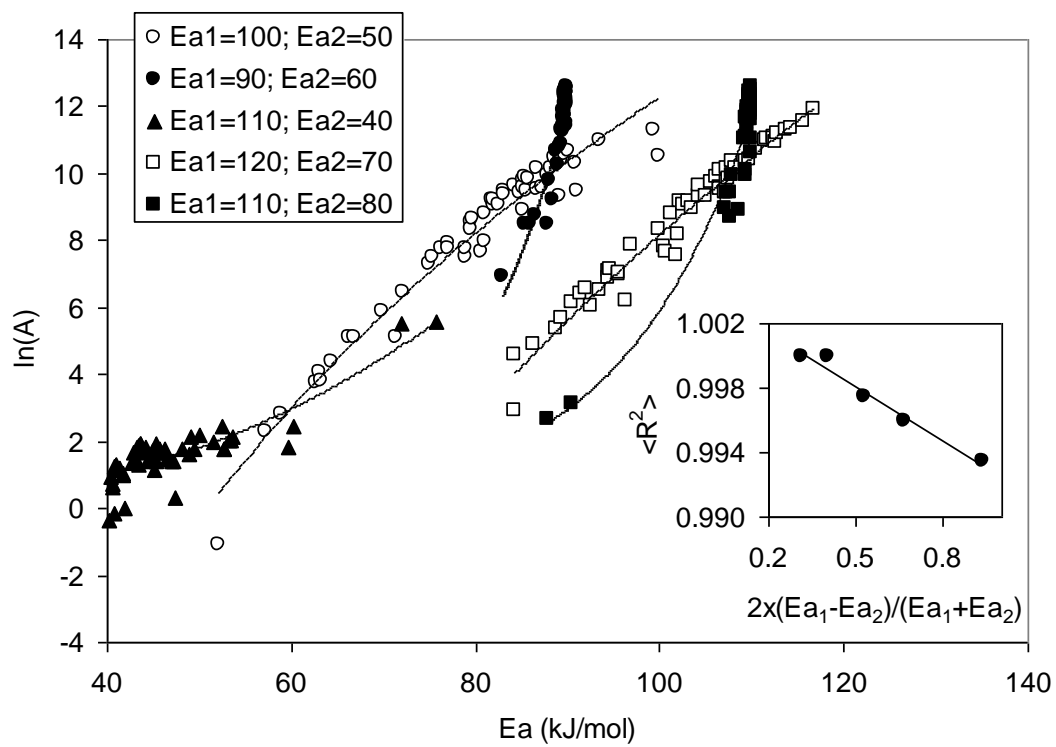
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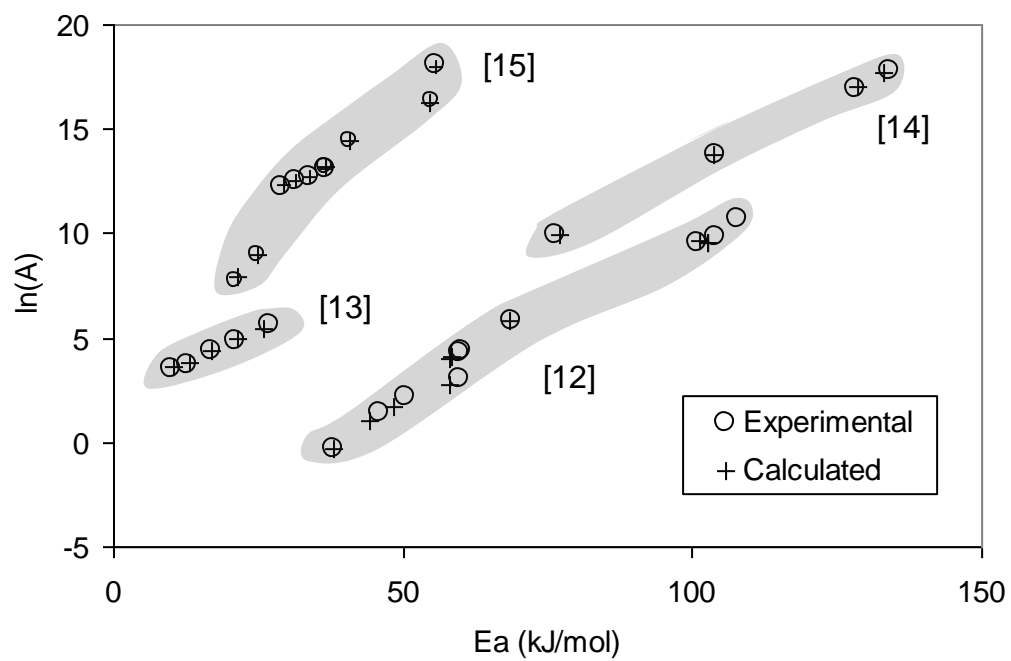
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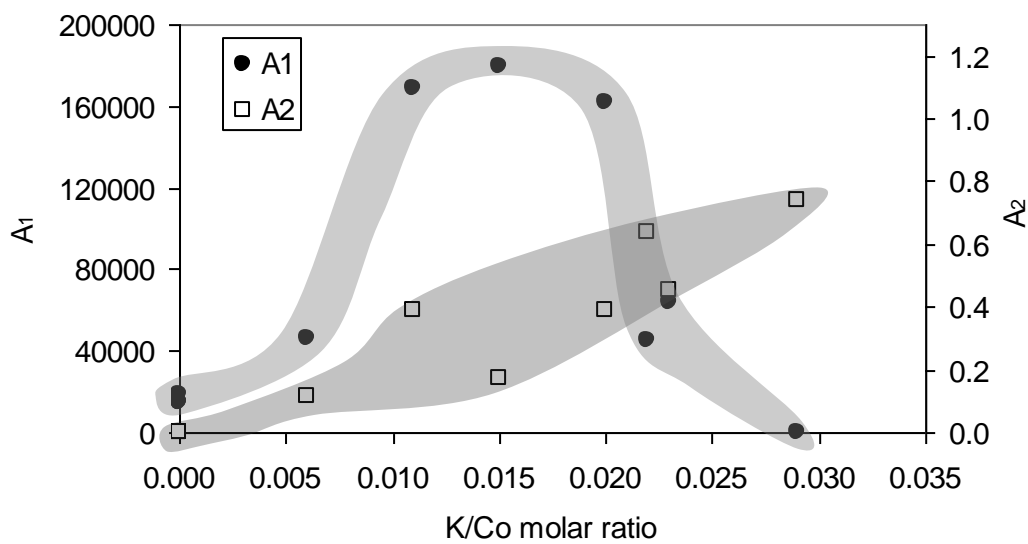
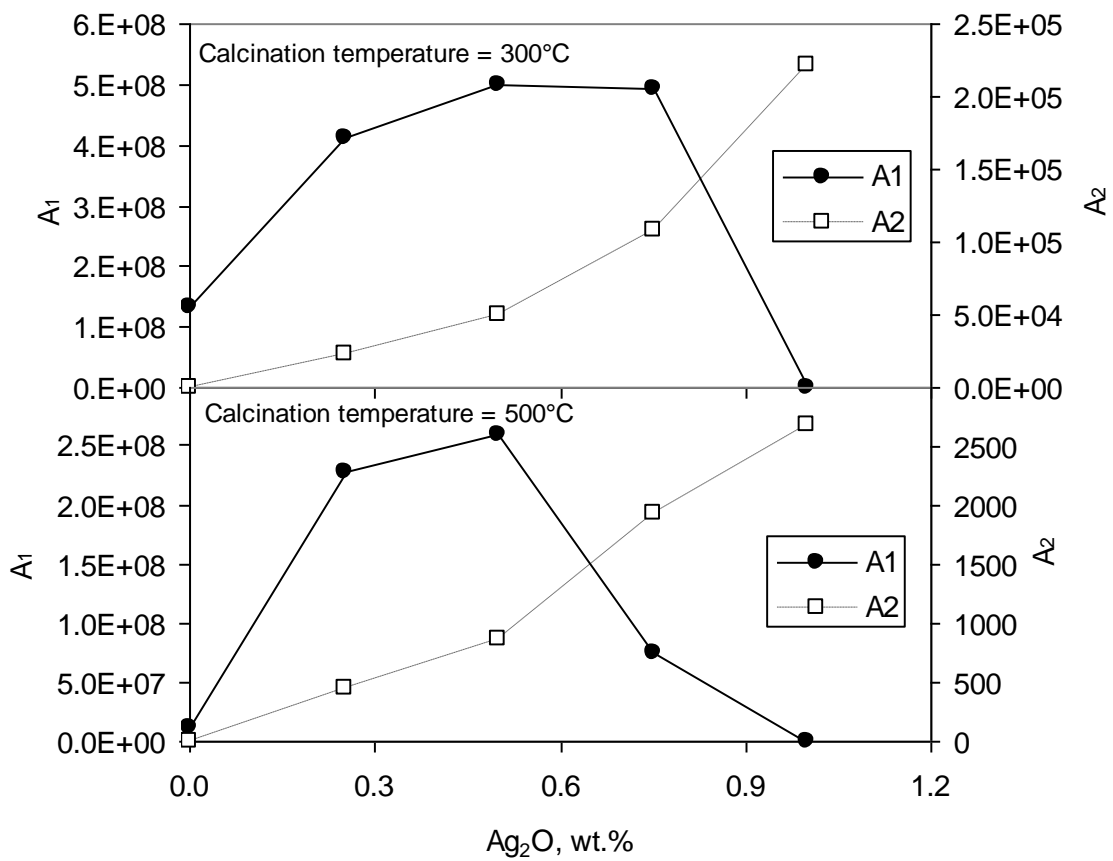Figure 3 (Laura del Río and Gregorio Marbán)
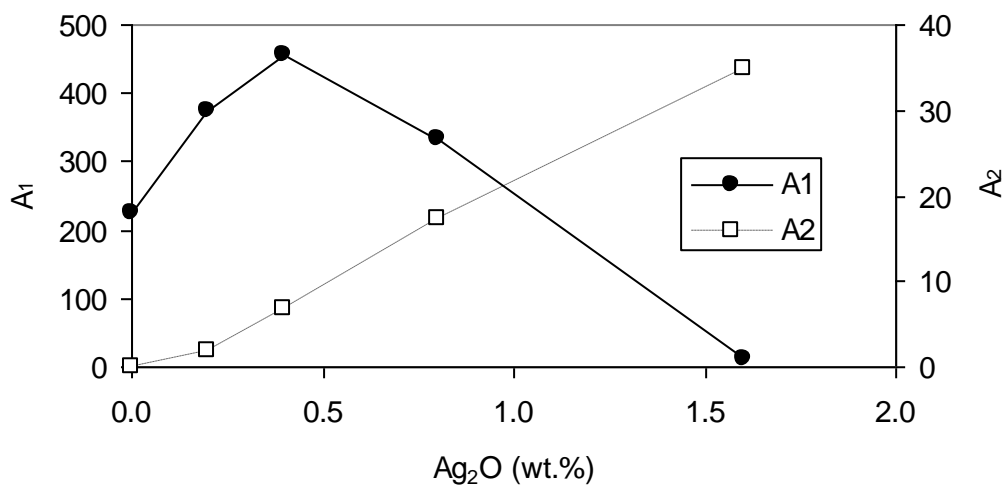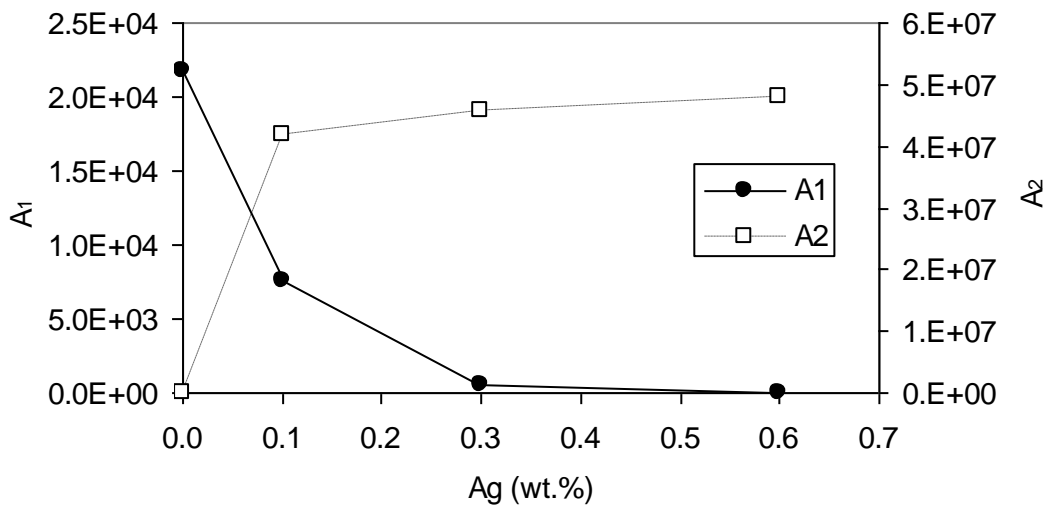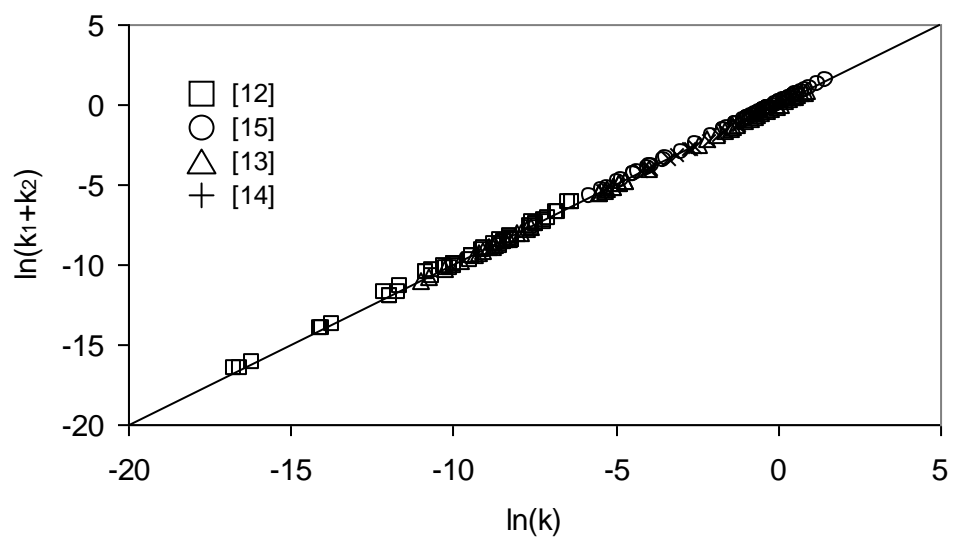
Figure 4 (Laura del Río and Gregorio Marbán)

Figure 5 (Laura del Río and Gregorio Marbán)

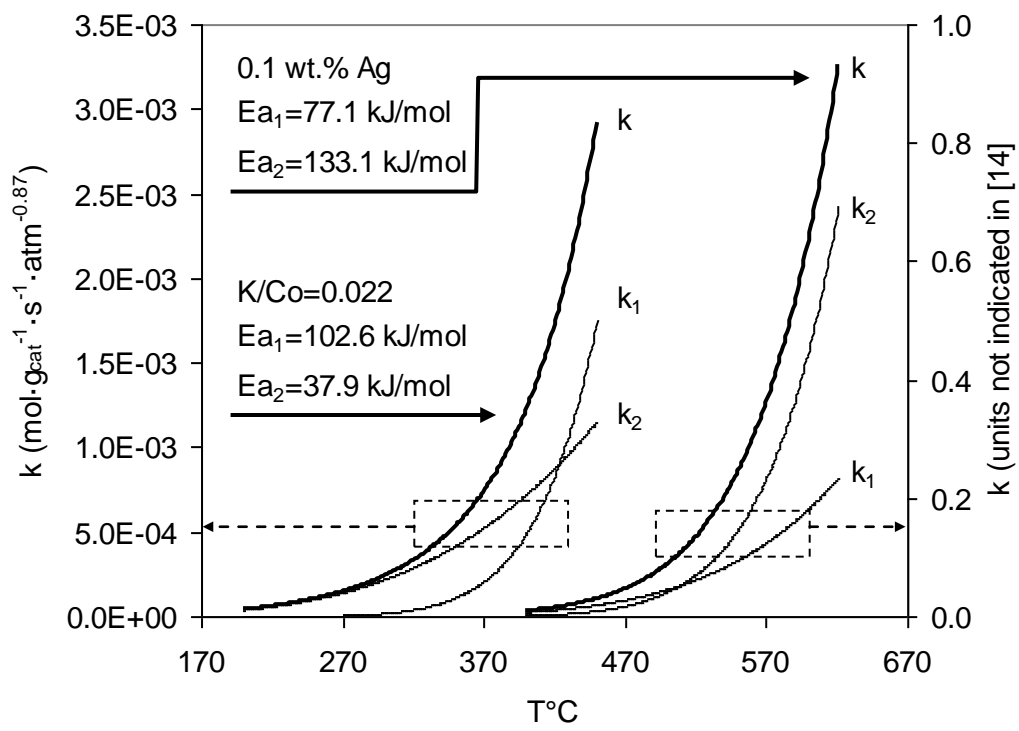Figure 6 (Laura del Río and Gregorio Marbán)

Figure 7 (Laura del Río and Gregorio Marbán)

Figure 8 (Laura del Río and Gregorio Marbán)